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Conformation and Dynamics of Polymers in Solution

Final Report

Ben Chu

June 11, 1982

U. S. Army Research Office

Contract #DAAG29 79 C 0069

Chemistry Department
State University of New York at Stony Brook

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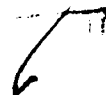
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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
	AD-A116629	
4. TITLE (and Subtitle)		5. TYPE OF REPORT & PERIOD COVERED
CONFORMATION AND DYNAMICS OF POLYMERS IN SOLUTION		Final Report 4/1/79-3/31/82
7. AUTHOR(s)		6. PERFORMING ORG. REPORT NUMBER
Ben Chu		5010C
9. PERFORMING ORGANIZATION NAME AND ADDRESS		8. CONTRACT OR GRANT NUMBER(s)
Chemistry Department State University of New York Stony Brook, New York		DAAG29 79 C 0069
11. CONTROLLING OFFICE NAME AND ADDRESS		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
U. S. Army Research Office Post Office Box 12211 Research Triangle Park, NC 27709		
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		12. REPORT DATE
		June 11, 1982
		13. NUMBER OF PAGES
		15. SECURITY CLASS. (of this report)
		Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report)		
Approved for public release; distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
NA		
18. SUPPLEMENTARY NOTES		
The view, opinions, and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number)		
Polymer Dynamics, Phase Transitions, Polymer Kinetics, Light Scattering.		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number)		

Foreward

I have been supported by the U.S. Army Research Office without interruption since 1963. The financial assistance and the long range goals of the program administrators including their patience and understanding are greatly appreciated. I have been working towards the improvements in instrumentation related to laser light scattering and its applications to polymer physics and am glad to report that the field has finally reached a stage capable of contributing towards the basic as well as applied aspects of polymer science.



AGP

Final Report

a. Statement of problems studied.

(i) To investigate the static and dynamical properties of polymers in solution from dilute to semidilute solutions using the scaling concept.

(ii) To examine the characterization of molecular polydispersity effects using photon correlation function analysis.

(iii) To study the temperature-composition behavior of a polymer solution, polystyrene in methyl acetate, which has an upper and a lower critical solution temperature.

(iv) To study polymerization kinetics by Raman scattering.

b. Summary of the most important results.

(i) We have shown that although the scaling concept is correct in the limit of infinite polymer molecular weight, its application needs to be modified for finite molecular weight polymers. In semidilute solution, the presence of pseudo gel high frequency motions can be analyzed by means of a histogram method of correlation function profile analysis.

(ii) In our characterization of molecular polydispersity, we must emphasize the interactive nature of experimental measurements, methods of data analysis, and comparison with theory. An empirical method was developed to approximate the Laplace inversion in order to estimate the linewidth distribution function. By taking into account the particle scattering factor and intermolecular interactions, we were able to determine the molecular weight distributions of polymers such as polystyrene, poly[bis(m-chlorophenoxy)phosphazene].

(iii) We have examined a polymer solution, polystyrene in methyl acetate PS/MA which has an upper and a lower critical solution temperature within the

experimental range of our light scattering spectrometer. The result of this investigation has led us to consider the PS/MA system as a possible candidate for studying the kinetics of spinodal decomposition and nucleation processes.

(iv) Raman scattering in combination with light scattering and refractive index measurements may permit us to develop a technique to study polymerization kinetics including the determination of polymer/monomer concentration, molecular weight and distribution of polymer, as well as polymer size. (See attached reprint and galley).

c. List of publications.

During the contract period (4/1/79-3/31/82) the following articles were published with the support of the U.S. Army Research Office.

102. Esin Gulari, Erdogan Gulari, Y. Tsunashima and B. Chu, Photon Correlation Spectroscopy of Particle Distributions, J. Chem. Phys., 70(8), 3965 (1979).
103. B. Chu, Dynamics of Macromolecular Solutions, Physica Scripta, 19, 458 (1979).
104. B. Chu, Esin Gulari and Erdogan Gulari, Photon Correlation Measurements of Colloidal Size Distributions. II. Details of Histogram Approach and Comparison of Methods of Data Analysis, Physica Scripta, 19, 476 (1979).
- 105.* B. Chu and T. Nose, Static and Dynamical Properties of Polystyrene in Transdecalin, Macromolecules, 12, 347 (1979).
106. Erdogan Gulari, Esin Gulari, Y. Tsunashima, and B. Chu, Polymer Diffusion in a Dilute Theta Solution: 1. Polystyrene in Cyclohexane, Polymer, 20, 347 (1979).
107. B. Chu and Esin Gulari, Polymer Diffusion in a Dilute Solution: 2. Poly[bis(m-chlorophenoxy)phosphazene] in chloroform, Macromolecules, 12, 445 (1979).
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123. A. DiNapoli, B. Chu, and T.Y. Liu, Light Scattering Spectroscopy of Meningococcal Polysaccharides, American Chemical Society Symposium Series, 150, (1981) pp 173-199.
124. Y.-H. Lin and B. Chu, Static and Dynamical Properties of Polystyrene in Carbon Tetrachloride. 1. Characteristic Frequency in the Dilute, Intermediate, and Semi-Dilute Regions, Macromolecules, 14, 385 (1981).
125. B. Chu and Y.-H. Lin, Static and Dynamical Properties of Polystyrene in Carbon Tetrachloride. 2. Osmotic Pressure and Radius of Gyration in the Dilute, Intermediate and Semi-Dilute Regions, Macromolecules, 14, 392 (1981).
126. B. Chu, G. Fytas, and G. Zalczer, Study of Thermal Polymerization of Styrene by Raman Scattering, Macromolecules, 14, 395 (1981).
128. G. Fytas, Th. Dorfmueller, Y.-H. Lin and B. Chu, Photon Correlation Spectroscopy of Bulk Siloxane Polymers, Macromolecules, 14, 1088 (1981).
129. Y.-H. Lin, G. Fytas and B. Chu, Depolarized Rayleigh Spectra of Siloxane Polymers, J. Chem. Phys. 75, 2091 (1981).

d. List of all participating scientific personnel.

Post -Doctorates:	Gilbert Zalczer	Kenji Kubota
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Graduate Students:	John Pope	
	W. Bujalowski	
	R. Lee	
Undergraduate:	Peter Chu	
Secretarial:	Jane Wainio	

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Study of Thermal Polymerization of Styrene by Raman Scattering

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Long Island, New York 11794. Received May 22, 1980

ABSTRACT: We present a new method for studying polymerization kinetics based on Raman scattering. Our method has selectivity, is reliable and easy to apply, can be automated, and is insensitive to most spurious phenomena. We demonstrate this method by a study of the thermal polymerization of styrene at 60, 75, and 90 °C.

Introduction

The thermal polymerization of styrene has recently been the subject of several studies by light-beating spectroscopy (polarized¹ and depolarized²), interferometry (polarized³ and depolarized⁴), and NMR.⁵ We present here a new method based on Raman scattering. Our method has selectivity, is reliable and easy to apply, can be automated, and involves little external calibration. We emphasize that, since polymerization involves changes in chemical bonds which can usually be observed through Raman lines, this technique should be applicable to almost any polymerization process.

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Principle and Calibration

The principle of the method is to record Raman spectra from the sample at different stages of polymerization. In a polymerization reaction some portion of the molecular structure of interest usually remains unchanged. The corresponding Raman-active lines are present throughout the process and can be used as standards to calibrate the intensity of other lines, while those related specifically to the monomer vanish and those related to the polymer grow. Monitoring a ratio of intensities makes the measurement insensitive to laser power fluctuations or sample turbidity. Therefore, the method is reliable even in unfavorable conditions. In particular, applications of the method for studying copolymerization processes should be a worthwhile extension.

The first step is to measure Raman spectra of the monomer and of the polymer and to select the useful lines. When many Raman peaks are present, some of this in-

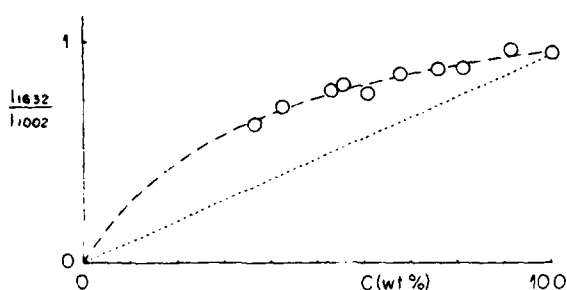


Figure 1. Ratio of the intensities of the 1632-cm⁻¹ (double bond) line to the 1002-cm⁻¹ (ring) line, I_2/I_1 , as a function of the monomer concentration: (---) equal-scattering hypothesis; (—) fit to eq 2.

formation is redundant. Consequently, there is no need to scan the entire Raman spectrum during kinetic studies. Furthermore, for many interesting polymers the spectra and assignments of both the monomers and the polymers are available in the literature. In our case we selected the 1632-cm⁻¹ line due to the aliphatic double bond (denoted by subscript 2) and the 1002-cm⁻¹ line due to a ring vibration (denoted by subscript 1) for our studies of thermal polymerization of styrene. A natural hypothesis is to consider the ring lines independent of the concentration. In other words, the Raman scattering due to the ring vibration remains the same whether it belongs to a monomer or to a polymer. Unfortunately, this is misleading. Indeed we measured the ratio of those lines in polystyrene in styrene solutions of different known polymer concentrations. The above assumption predicts straight-line behavior, obviously not verified by the data, as shown in Figure 1.

Let c_m be the concentration of monomer molecules and c_p be that of polymer segments in a unit volume. The intensity due to the aliphatic double bond is $I_2 = a_2 c_m$ and that due to the ring is $I_1 = a_1 c_m + b_1 c_p$, where $a_1 \neq b_1$. So we get

$$\frac{I_2}{I_1} = \frac{a_2 c_m}{a_1 c_m + b_1 c_p} \quad (1)$$

If the concentrations appear only as ratios, we can use mass concentrations and normalize them so that $c_m + c_p = 1$. Then we have the empirical expression

$$\frac{I_2}{I_1} = \frac{a_2}{a_1} \left[\frac{1}{b_1/a_1 + (1 - b_1/a_1)c_m} \right] \quad (2)$$

The equations are insensitive to density changes. The ratio a_2/a_1 is equal to I_2/I_1 when $c_m = 1$. The ratio b_1/a_1 can be deduced from a fit of the calibration data in Figure 1. The upper curve in Figure 1 represents a good agreement between eq 2 and our calibration using $a_2/a_1 = 1.32 \pm 0.06$ and $b_1/a_1 = 0.59 \pm 0.04$. The first of these ratios has a weak temperature dependence but the second, corresponding to lines at the same frequency, can be assumed constant and is essentially independent of the optical alignment of the Raman spectrometer. For more complex systems, other empirical formulas can be developed. In any case, a calibration is essential in order to achieve quantitative results.

Thermal Polymerization of Styrene

We have applied this technique to the thermal polymerization of styrene, using a Spex 1302 double-monochromator (0.5 m, 1200 grooves/mm) and recording the spectra by means of a chart recorder. As we were interested mainly in the integrated intensities of the peaks, we could use wide slits ($\sim 300 \mu\text{m}$), which reduce the required laser power

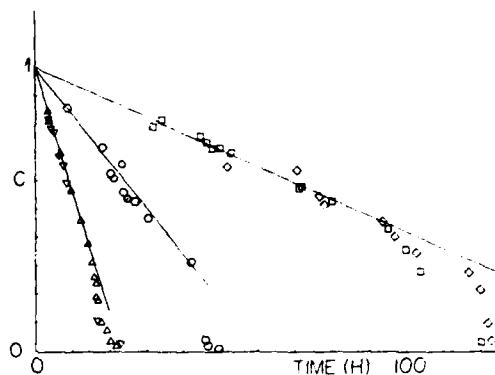


Figure 2. Concentration of monomer vs. time: (∇ , Δ) cells 1 and 4, 90 °C; (\circ , \odot) cells 2 and 5, 75 °C; (\square , \diamond) cells 3 and 6, 60 °C. H = hour.

Table I

	temperature, °C		
	60	75	90
initial rate, %/h	0.32	1.1	3.1

($\sim 300 \text{ mW}$ at 488 nm) and thence the occurrence of any photoactivated process. In fact, a spectrometer of much poorer quality would have been sufficient. On the other hand, refinements such as computer-controlled scan, digital recording, and automatic data acquisition can be introduced easily. We are in the process of making our experiments fully automatic.

Among the six samples we have studied, five were only degassed by several freeze-pump cycles, the inhibitor (*tert*-butylpyrocatechol) being left undisturbed. The sixth one was washed several times with water in order to remove the inhibitor and then dried, first with calcium chloride and then with calcium hydride. The observed rate of polymerization for that cell (no. 1) agrees quite well with the other measurements. We ran two samples at each of three temperatures, 60, 75, and 90 °C, and found good reproducibility in our measurements. The concentration of monomer vs. time is reported in Figure 2 for all cells. We find a linear behavior until about 65% of the reaction, where it suddenly becomes faster. Such a behavior, known as the Trommsdorff effect,⁶ has been observed by light scattering techniques.⁴ It is not clear yet whether this is a real phenomenon or an experimental artifact. Indeed when the viscosity of the sample becomes very high, the portion lighted is no longer renewed so the effect of several hundred milliwatts of light may no longer be negligible. In that region we have actually observed a thermal lens effect which has persisted hours after stopping the beam, but we cannot yet ascertain whether this effect is the reason for the change in the kinetics. Another possible reason for the acceleration in the polymerization kinetics is due to a decrease of the termination rate constant, in terms of intrachain interactions⁶ and chain-transfer effect,⁷ through tremendous viscosity increases during the polymerization process.

From the results of Figure 2, we can infer a variation of the initial rate with the temperature, as listed in Table I. The results are very well described by an Arrhenius law with an activation energy of 19 kcal/mol, the same as observed by classical methods,⁸ as can be seen in Figure 3. On the other hand, the rates we found are about 3 times higher than usually reported. We believe this disagreement is possibly due to sample preparation procedures and not the observation method. In order to check the Raman detection method, we polymerized an additional styrene

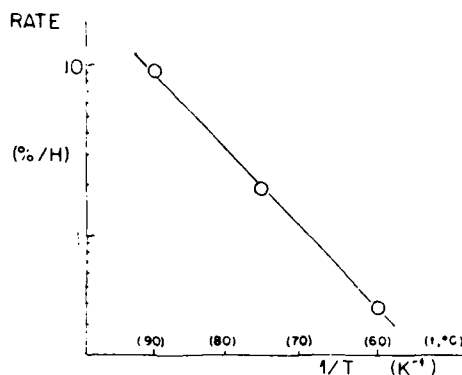


Figure 3. log of the initial reaction rate vs. reciprocal temperature. The solid line represents an Arrhenius law with an activation energy of 19 kcal/mol. H = hour.

sample at 75 °C for 19 h, during which time we monitored the monomer concentration, as shown typically in Figures 1 and 2. After stopping the reaction, we determined the polymer conversion classically by first dissolving the polymerized sample in 1,4-dioxane and then precipitating the polystyrene in methyl alcohol.⁸ We found an 18% conversion by the classical method and a 21% conversion based on Raman scattering. The agreement is quite reasonable, especially in view of the fact that there must be a residual amount of oligomers which are not precipitated by the classical method.

Conclusion

We have presented a new method for studying polym-

erization reactions based on Raman scattering. This method is fairly general, easy to use and to automate, and insensitive to most spurious phenomena. We have illustrated this method by a study of the thermal polymerization of styrene at different temperatures and found our results to be in essential agreement with those obtained by other methods.

Acknowledgment. We gratefully acknowledge support from the U.S. Army Research Office. G.Z. gratefully acknowledges support from Conseiller Culturel de l'Ambassade de France and the Service de l'Enseignement et des Echanges Linguistiques—Ministère des Affaires Etrangères (Paris). We thank Day-Chyuan Lee for his help in performing the Raman studies and the chemical analysis on the polystyrene content and Kirk J. Abbey for a helpful discussion.

References and Notes

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- (8) See, e.g.: Boundy, R. H.; Boyer, R. F., Eds. "Styrene, Its Polymers, Copolymers and Derivatives"; Hofner Publishing Company: New York, 1952.

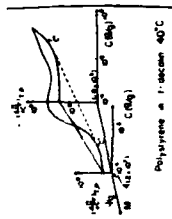


Figure 1. Sublimation representation of a three-dimensional plot of the relative concentration of the monomer as a function of the monomer concentration. The plot shows a series of curves representing different monomer concentrations, with the y-axis labeled 'C (M)' and the x-axis labeled 'C (M)'.

at

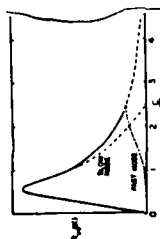


Figure 2. Sublimation representation of $D (M)$ as a function of the monomer concentration. The plot shows a series of curves representing different monomer concentrations, with the y-axis labeled 'D (M)' and the x-axis labeled 'C (M)'.

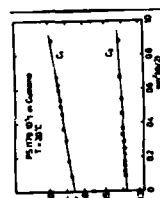


Figure 3. Plot of $D (M)$ vs. $C (M)$ for polypropylene (NBS 700). The plot shows a series of curves representing different monomer concentrations, with the y-axis labeled 'D (M)' and the x-axis labeled 'C (M)'.

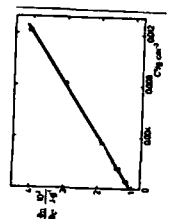


Figure 4. Plot of $D (M)$ vs. $C (M)$ for polypropylene (NBS 700). The plot shows a series of curves representing different monomer concentrations, with the y-axis labeled 'D (M)' and the x-axis labeled 'C (M)'.



Figure 5. Plot of $D (M)$ vs. $C (M)$ for polypropylene (NBS 700). The plot shows a series of curves representing different monomer concentrations, with the y-axis labeled 'D (M)' and the x-axis labeled 'C (M)'.

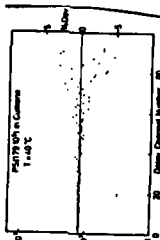


Figure 6. Plot of $D (M)$ vs. $C (M)$ for polypropylene (NBS 700). The plot shows a series of curves representing different monomer concentrations, with the y-axis labeled 'D (M)' and the x-axis labeled 'C (M)'.

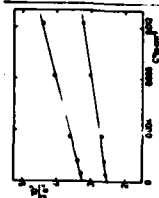


Figure 7. Plot of $D (M)$ vs. $C (M)$ for polypropylene (NBS 700). The plot shows a series of curves representing different monomer concentrations, with the y-axis labeled 'D (M)' and the x-axis labeled 'C (M)'.



Figure 8. Plots of $(\delta\epsilon/\delta C)_{T,p}$ vs. concentrations for polystyrene (filled ∇ 's) and α -methylstyrene (open ∇ 's) at 14.3 $^{\circ}\text{C}$ (filled circles) and 40 $^{\circ}\text{C}$ (open triangles). The two curves cross each other near the zero concentration limit because $\Delta\epsilon$ decreases with increasing concentration. In a plot of $(\delta\epsilon/\delta C)_{T,p}/RT$ vs. C , the two curves nearly meet at $C = 0$.



Figure 5. Plots of $1/\bar{R}_w$ vs. $\ln^2 \theta/23$ for polystyrenes (polymers 1, $M_n \sim 1.6 \times 10^4$) in toluene at 25°C. $C_1 = 4.37 \times 10^{-4}$ g/cm³ and $C_2 = 1.04 \times 10^{-2}$ g/cm³.

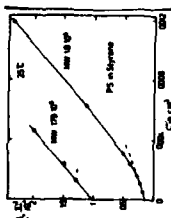


Figure 10. Plots of $(\partial\epsilon/\partial C)^{1/2}$ vs. concentration for polystyrene copolymers A and B) in acetone at 25 °C. The initial slope and an intercept of the linear curve yield $A_0 = 1.7 \times 10^4$ (cm³ mol)^{1/2} and $M_0 = 1.7 \times 10^5$ g/mol.

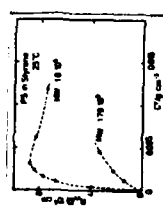
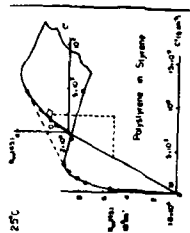


Figure 11. Plots of $\Delta_{\text{m}}H$ vs. C for polypropylene in toluene at 25°C.



1 Figures 12. Schematic representations of a three-dimensional net
2 of the Rughigh ratio $R_{gh} = dR^2$ as a function of molecular weight
3 and concentration for polyurethanes in toluene at 25 °C using data
4 of Figure 11.

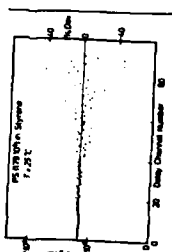


Figure 12. Plot of $\text{Alg}^{2+} \cdot 10^6$ m. delay channel number / for polystyrene (NBS 705 standard) in styrene at $C = 0.04 \times 10^{-2}$ g./g. β 20, $t = 25^\circ\text{C}$, and $\Delta r = 0.4$ μ . By using the correlation method.

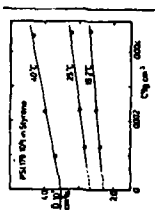


Figure 14. Plots of D (cm^2/K^2) vs. concentration for NBS 703 standard polystyrene in acetone at 14.3, 24, and 40 $^{\circ}\text{C}$.

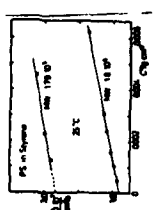


Figure 11. Plots of D (cm^2/K^2) vs. concentrations for polystyrene.

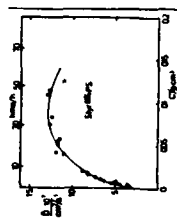


Figure 20. Plot of D (wt/%) vs. polymerization time and temperature. The curves represent the polymerization of $CH_2=CH_2$ at 100°C and 120°C.

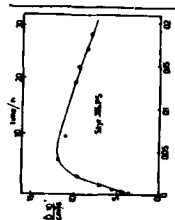


Figure 21. Plot of D (wt/%) vs. polymerization time and temperature. The curves represent the polymerization of $CH_2=CH_2$ at 100°C and 120°C.

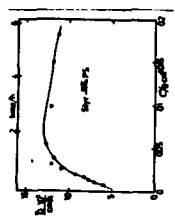


Figure 22. Plot of D (wt/%) vs. polymerization time and temperature. The curves represent the polymerization of $CH_2=CH_2$ at 100°C and 120°C.

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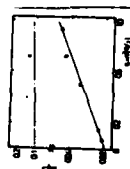


Figure 14. Plot of polymerization rate vs. temperature. The curve represents the polymerization of $CH_2=CH_2$ at 100°C and 120°C.

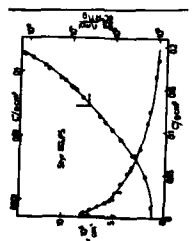


Figure 15. Plot of D (wt/%) vs. polymerization time and temperature. The curves represent the polymerization of $CH_2=CH_2$ at 100°C and 120°C.

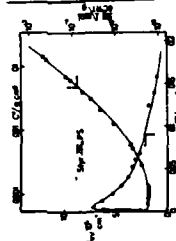


Figure 16. Plot of D (wt/%) vs. polymerization time and temperature. The curves represent the polymerization of $CH_2=CH_2$ at 100°C and 120°C.

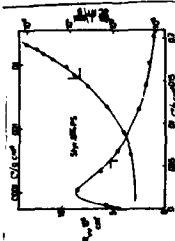


Figure 17. Plot of D (wt/%) vs. polymerization time and temperature. The curves represent the polymerization of $CH_2=CH_2$ at 100°C and 120°C.

[illegible]

* Tamura, J. "Physicochemical Constants of Pure Organic Compounds," Elsevier Publishing Co., New York, 1964, Vol II. * Soudry, B. M., Boye, R. P., Eds., "Styrene, Its Polymers, Copolymers, and Derivatives," McGraw-Hill Publishing Co., New York, 1965.

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temp., °C	current, g/cm ²	I_{A} , A	A_{eff} (cm ²)	ΔE , mV	$\frac{dI}{dE}$, A/V
30	6.06×10^{-4}	170	4.9×10^{-4}	181	181
30	1.46×10^{-3}	145	4.9×10^{-4}	181	181
30	infinite diffusion	160 (by extrapolation)	4.9×10^{-4}	181	181
40	6.06×10^{-4}	175	4.7×10^{-4}	186	(178)
40	1.19×10^{-3}	144	4.7×10^{-4}	186	(178)
40	infinite diffusion	160 (by extrapolation)	4.7×10^{-4}	186	186

• Equations 1 & 2

Temp., °C	[η] (dl/g)		[η] (dl/g)
	in CHCl ₃	in CH ₂ Cl ₂	
25	0.45	0.45	0.45
35	0.45	0.45	0.45
45	0.45	0.45	0.45
55	0.45	0.45	0.45
65	0.45	0.45	0.45
75	0.45	0.45	0.45
85	0.45	0.45	0.45
95	0.45	0.45	0.45
105	0.45	0.45	0.45
115	0.45	0.45	0.45
125	0.45	0.45	0.45
135	0.45	0.45	0.45
145	0.45	0.45	0.45
155	0.45	0.45	0.45
165	0.45	0.45	0.45
175	0.45	0.45	0.45
185	0.45	0.45	0.45
195	0.45	0.45	0.45
205	0.45	0.45	0.45
215	0.45	0.45	0.45
225	0.45	0.45	0.45
235	0.45	0.45	0.45
245	0.45	0.45	0.45
255	0.45	0.45	0.45
265	0.45	0.45	0.45
275	0.45	0.45	0.45
285	0.45	0.45	0.45
295	0.45	0.45	0.45
305	0.45	0.45	0.45
315	0.45	0.45	0.45
325	0.45	0.45	0.45
335	0.45	0.45	0.45
345	0.45	0.45	0.45
355	0.45	0.45	0.45
365	0.45	0.45	0.45
375	0.45	0.45	0.45
385	0.45	0.45	0.45
395	0.45	0.45	0.45
405	0.45	0.45	0.45
415	0.45	0.45	0.45
425	0.45	0.45	0.45
435	0.45	0.45	0.45
445	0.45	0.45	0.45
455	0.45	0.45	0.45
465	0.45	0.45	0.45
475	0.45	0.45	0.45
485	0.45	0.45	0.45
495	0.45	0.45	0.45
505	0.45	0.45	0.45
515	0.45	0.45	0.45
525	0.45	0.45	0.45
535	0.45	0.45	0.45
545	0.45	0.45	0.45
555	0.45	0.45	0.45
565	0.45	0.45	0.45
575	0.45	0.45	0.45
585	0.45	0.45	0.45
595	0.45	0.45	0.45
605	0.45	0.45	0.45
615	0.45	0.45	0.45
625	0.45	0.45	0.45
635	0.45	0.45	0.45
645	0.45	0.45	0.45
655	0.45	0.45	0.45
665	0.45	0.45	0.45
675	0.45	0.45	0.45
685	0.45	0.45	0.45
695	0.45	0.45	0.45
705	0.45	0.45	0.45
715	0.45	0.45	0.45
725	0.45	0.45	0.45
735	0.45	0.45	0.45
745	0.45	0.45	0.45
755	0.45	0.45	0.45
765	0.45	0.45	0.45
775	0.45	0.45	0.45
785	0.45	0.45	0.45
795	0.45	0.45	0.45
805	0.45	0.45	0.45
815	0.45	0.45	0.45
825	0.45	0.45	0.45
835	0.45	0.45	0.45
845	0.45	0.45	0.45
855	0.45	0.45	0.45
865	0.45	0.45	0.45
875	0.45	0.45	0.45
885	0.45	0.45	0.45

$T^{\circ}\text{C}$	$D^{\circ}\text{cm}^2\text{s}^{-1} \times 10^{-7}$	$\rho^{\circ}\text{g cm}^{-3}$	$\eta^{\circ}\text{cm}^2\text{s}^{-1} \times 10^{-4}$	$\eta_{sp}/c^{\circ}\text{cm}^2\text{s}^{-1} \times 10^{-4}$	$\eta_{sp}/c^{\circ}\text{cm}^2\text{s}^{-1} \times 10^{-4}$
25	2.61	1.01	90	2.60	0.64
30	2.40	0.98	80	2.39	0.64
35	2.19	0.95	70	2.18	0.64
40	1.98	0.92	60	1.97	0.64
45	1.77	0.89	50	1.76	0.64
50	1.56	0.86	40	1.55	0.64
55	1.35	0.83	30	1.34	0.64
60	1.14	0.80	20	1.13	0.64
65	0.93	0.77	10	0.92	0.64

Topic: The effects of climate change on coastal ecosystems.

Polymers A: NBS 700 Standard, $M_w = 1.79 \times 10^5$

	18.2	25	40
$M, (\text{cm}^3 \text{ mol})/g^a \times 10^{-4}$	6.0	5.97	5.91
$M_w, (\text{cm}^3 \text{ mol})/g^a \times 10^{-4}$	4.6	4.2	3.7
$M_n, (\text{cm}^3 \text{ mol})/g^a \times 10^{-4}$	3.4	2.4	2.6

L. A	434	409	10.4
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Parameters at 25 °C.